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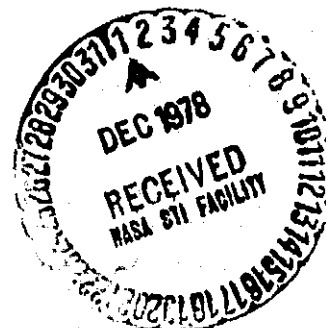
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A STUDY OF VARIOUS SYNTHETIC
ROUTES TO PRODUCE A HALOGEN-
LABELED TRACTION FLUID

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SUMMARY

Several synthetic routes were studied for the synthesis of the compound 1, 1, 3-trimethyl-1, 3-dicyclohexyl-2-chloropropane. This halogen-labeled fluid would be of use in the study of high traction lubricants (i. e., fluids which exhibit high coefficients of friction). This compound was to be used as an indicator of fluid molecular alignment in elastohydrodynamic contacts. Alignment would be detected by determining the direction of the carbon-chlorine bond moment using polarized infrared emission spectra.

The synthetic routes investigated were:

- (1) A dimerization of α -methylstyrene.
- (2) Copper (I) promoted addition of methanol to α -methylstyrene.
- (3) A Wittig reaction and
- (4) An organometallic approach

Because of steric hindrance and competing reactions, none of these synthetic routes were successful. It was concluded that this compound could not be easily synthesized and that a less complicated halogenated structure be considered.

INTRODUCTION

The increased interest in traction drives for power transmission is causing a demand for improved high traction lubricants (i. e., fluids which exhibit high coefficients of friction (ref. 1). Present lubricants for these applications have been empirically developed since their mechanism of operation is unknown (ref. 2). Recent studies (refs. 3 to 5) have begun to elucidate how these lubricants function in elastohydrodynamic contacts. In another study (ref. 6) infrared emission spectroscopy is being used to determine the chemical and physical states of lubricants elastohydrodynamic conditions.

It was felt that a halogenated compound, similar in structure to the traction lubricants, would provide further information in the above spectroscopic study. In particular, a chlorinated compound was considered because the direction of the carbon-chlorine bond moment could be determined from polarized infrared spectra. Then, in principle, molecular fluid alignment in an elastohydrodynamic contact could be determined from these measurements.

Therefore, the objective of this study was to synthesize the chlorinated compound, 1, 1, 3-trimethyl-1, 3-dicyclohexyl-2-chloropropane. The synthetic routes studied were: (1) a dimerization of α -methylstyrene, (2) copper (I) promoted addition of methanol to α -methylstyrene, (3) a Wittig reaction, and (4) an organometallic approach.

RESULTS AND DISCUSSION

Proposed Halogenated Compound

The proposed halogenated compound to be used as an indicator fluid in infrared emission spectroscopy studies on elastohydrodynamic contacts is shown in figure 1. This cycloaliphatic hydrocarbon is structurally similar to the high traction components used in high traction lubricants. Its chemical name is: 1, 1, 3-trimethyl-1, 3-dicyclohexyl-2-chloropropane.

Several methods for synthesis were attempted. Figures 2 and 3 summarized representative syntheses performed and the expected products.

Dimerization of α -Methylstyrene

The dimerization of α -methylstyrene (II) gave numerous products. A minimum of six different α -methylstyrene dimers formed in acid have been isolated in small quantities and analyzed by NMR (ref. 7). The lack of specificity of this reaction and the problems associated with the chromatographic isolation of the desired dimer from the many other products formed led us to abandon this route (fig. 2(a), II-IV).

Copper (I) Promoted Addition of Methanol to α -Methylstyrene

When α -methylstyrene was treated with acid and CuCl , 2-phenyl-2-methoxypropane (III) was formed, but in very poor yield as determined by thin layer chromatography (fig. 2(b), II-III). Routes employing α -methylstyrene were therefore judged to be unsatisfactory.

Wittig Reaction

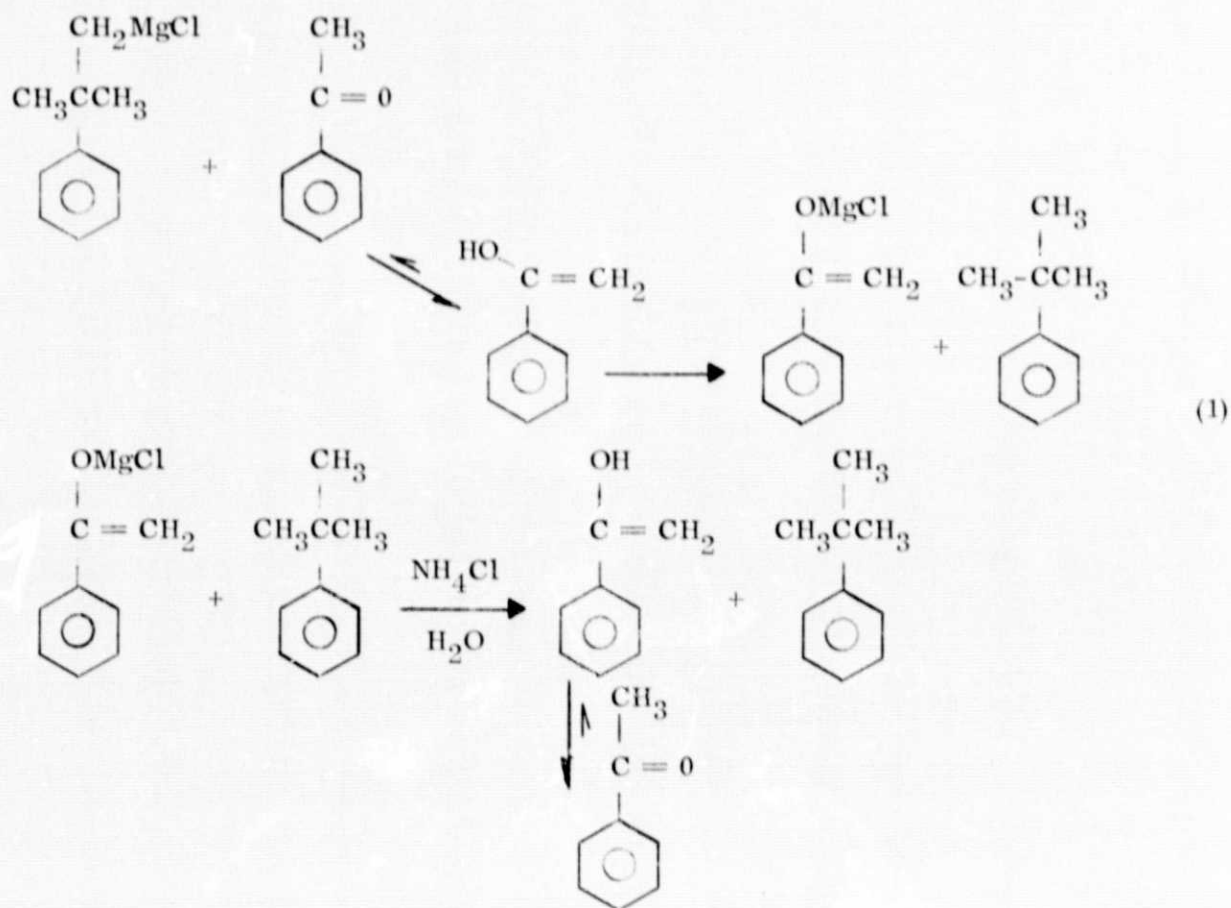
The Wittig reaction is very useful for the synthesis of olefins. Typically, an appropriately substituted ylid is reacted with an aldehyde or ketone. In this study (fig. 2(c), α -phenylisobutyraldehyde (α -methylhydratropaldehyde, VIII) and sec-phenethyltriphenylphosphonium iodide (V) were required. To obtain α -phenylisobutyraldehyde (VIII), mandelic acid (VI) was esterified in >80 percent yield; this was followed by treatment with methylmagnesium iodide to give the diol (VII) in ~65 percent (ref. 8). Using formic acid as a rearrangement medium (ref. 9) the aldehyde (VIII) was isolated in 83 percent of theory (fig. 2(c), VII-VIII).

Sec-phenethyl chloride (IX) did not react with triphenylphosphine, even under forcing conditions; however, sec-phenethyl iodide (X) readily formed the desired

phosphonium salt (V) (fig. 2(c), X-V). Treatment of the phosphonium salt (V) with *n*-butyllithium gave a blood-red color in THF; but addition of the aldehyde (VIII) to the ylid, even when followed by refluxing, gave an incomplete reaction as evidenced by the chromatographic recovery of unreacted aldehyde and phosphonium salt. Work-up by vacuum distillation of the organic products resulted in polymerization in the pot. The outcome of these experiments demonstrates that steric hindrance seriously impairs the Wittig approach to the desired olefin.

Organometallic Approach

An organometallic strategy (fig. 3) was developed, since, in general, organometallics are less sensitive to steric factors. Neophyl chloride (XI) (ref. 10), prepared in 74 percent yield, was converted to neophylmagnesium chloride and reacted with acetophenone. More than 55 percent of unreacted acetophenone was recovered by vacuum distillation in addition to several other fractions, all of which gave negative chromic anhydride and ceric nitrate tests for the hydroxyl function. The lack of normal 1,2 addition here may perhaps be attributed to steric hindrance, such that enolization of the ketone is preferred over normal addition as illustrated by equation (1):



To avoid this problem, neophyl lithium (XII) (ref. 11) was reacted with acetophenone (fig. 3). Unfortunately, this reaction mixture solidified on warming indicating polymerization. Again, no hydroxylic products were formed. Alternately, sec-phenethyl lithium (XIII) was prepared and was reacted with α -phenylisobutyraldehyde (VIII). The predominant product here seemed to be styrene as noted by its characteristically pungent odor. Once again, an undesired reaction, in this case elimination, seemed to be favored over 1, 2-addition.

It was recognized at the outset that the synthesis of the desired intermediate olefin would be difficult because of the obvious steric factors. For this reason when the Wittig reaction failed, the organometallic route was pursued, since organometallics are in general less sensitive to steric factors (fig. 3, XI-I).

SUMMARY OF RESULTS

Several synthetic routes were studied for synthesis of the compound, 1, 1, 3-trimethyl-1, 3-dicyclohexyl-2-chloropropane. This compound was to be used as an indicator of fluid molecular alignment in elastohydrodynamic studies of high traction lubricants using infrared emission spectroscopy. The routes studied were: (1) a dimerization of α -methylstyrene, (2) copper (I) promoted addition of methanol to α -methylstyrene, (3) a Wittig reaction, and (4) an organometallic approach. The major results were:

1. None of the synthetic routes were successful because of competing reactions or steric hindrance.
2. It was concluded that this compound could not be easily synthesized and that a less complicated halogenated structure be considered.

ACKNOWLEDGEMENT

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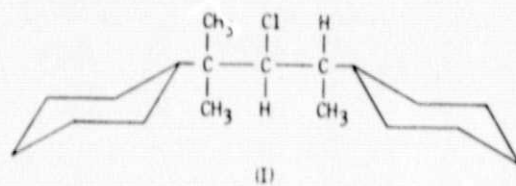
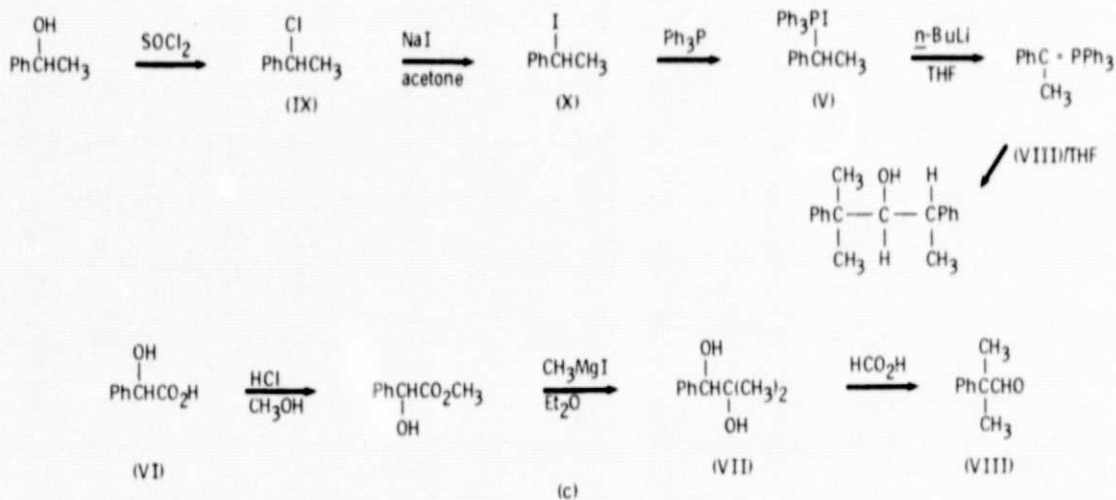


Figure 1. - Proposed halogenated traction compound
 (1, 1, 3-trimethyl-1, 3-dicyclohexyl-2-chloropropane).



(b) Copper (I) promoted addition of methanol to α -methyl styrene.

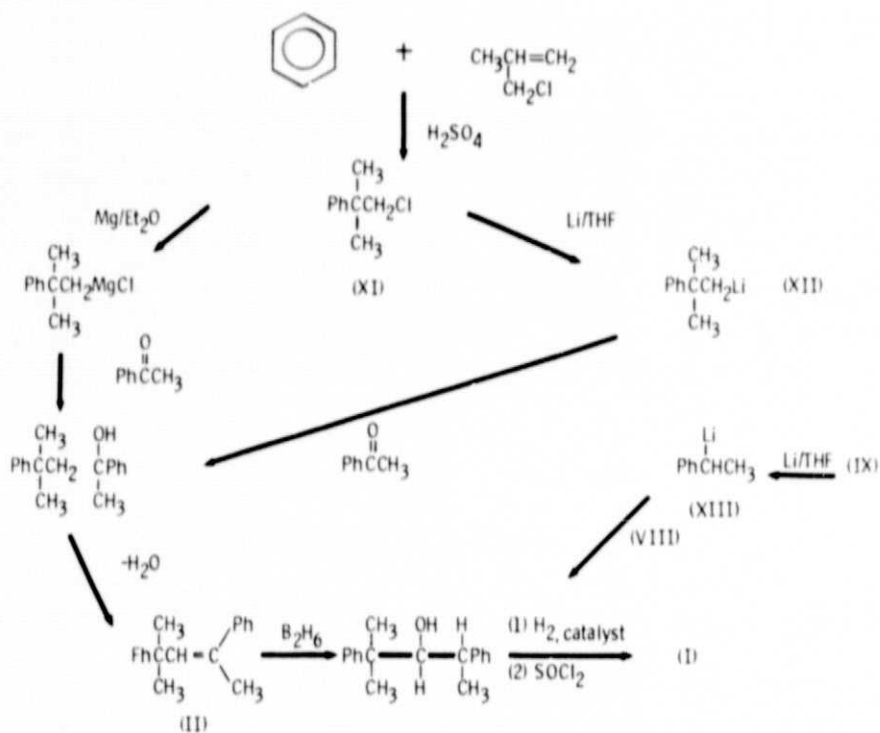


Figure 3. - Flow chart of reactions and expected products for organometallic approach.